

Susceptibility of Welded and Non-Welded Titanium Alloys to Environmentally Assisted Cracking in Simulated Concentrated Ground Waters

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SUSCEPTIBILITYOFWELDEDANDNON -WELDEDTITANIUMALLOYS TOENVIRONMENTALLYASSISTEDCRACKING INSIMULATEDCO NCENTRATEDGROUNDWATERS

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ABSTRACT

The engineering barriers for the nuclear waste repository at Yucca Mountain include a double walled container and a detached dripshield. The material selected to construct the dripshield will be Tit anium Grade7(TiGr7orR52400). TiGr7ishighlyresistanttocorrosionandconsequentlyitiswidelyused to handle aggressive industrial envir on ments. The model for the degradation of the eng ineeringbarriers includes three modes of corrosion, namely general corrosion, l ocalized corrosion and environmentally assisted cracking (EAC). The objective of the current research was to characterize the s usceptibilityof threetitaniumalloystoEACinseveralenvironmentalcond itions with varying solution composition, pH and temperature. The suscept ibility to EAC was evaluated using constant deformation (deflection) U -welded and welded cond itions. Results show that after more than five bend specimens in both the non yearsexposureinthevaporandliquidphasesofalkaline(pH~10)andacidic(pH~3)multi -ionicenv ironments at 60°C and 90°C, most of the specimens were free from EAC. The only specimens t hatsu ffered EAC were welded Ti Gr 12 (R53400) exposed to li quid simulated concentrated water (SCW) at 90°C.

Keywords: high -level nuclear waste, titanium alloys, R52400, R52402, R53400, environmentally a sisted cracking, U -bend, welded specimens, tempera ture, simulated acidified water (SAW), simulated concentratedwater (SCW), simulated dilutewater (SDW).

INTRODUCTION

ThecurrentwastepackagedesignfortheYuccaMountainProjectconsistsoftwoconcentricmetalco ntainersandadetacheddripshie ld. ^{1,2}Type316Lstainlesssteel(S31603)isthespecifiedmaterialforthe internal barrierorshell of the container, to act as a shield to radiation and to provide mechanical integration generally and the container of the

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rity. Alloy 22 (N06022) is the candidate material for the external bar rieror shell of the container. The primary purpose of the outer container is to provide protection against corrosion. Alloy 22 (N06022) was selected for this application because it is well known commercially for its excellent corrosion resistance in against corrosion. Alloy 22 (N06022) was selected for this application because it is well known commercially for its excellent corrosion resistance in against corrosion. Alloy 22 (N06022) was selected for this application because it is well known commercially for its excellent corrosion resistance in against corrosion. Alloy 22 (N06022) was selected for this application of the variety against corrosion. Alloy 22 (N06022) was selected for this application of the variety against corrosion. Alloy 22 (N06022) was selected for this application of the variety against corrosion. Alloy 22 (N06022) was selected for this application of the variety against corrosion. Alloy 22 (N06022) was selected for this application of the variety against corrosion. Alloy 22 (N06022) was selected for this application because it is well known commercially for its excellent corrosion. Alloy 22 (N06022) was selected for this application because it is well known commercially for its excellent corrosion. Alloy 22 (N06022) was selected for this application because it is well known commercially for its excellent corrosion. Alloy 22 (N06022) was selected for the variety against corrosion. Alloy 22 (N06022) was selected for the variety against corrosion. Alloy 22 (N06022) was selected for the variety against corrosion. Alloy 22 (N06022) was selected for the variety against corrosion. Alloy 22 (N06022) was selected for the variety against corrosion. Alloy 22 (N06022) was selected for the variety against corrosion. Alloy 22 (N06022) was selected for the variety against corrosion against corrosion. Alloy 22 (N06022) was selected for the variety against corrosion against corrosion against corrosion. Alloy 22 (N06022) was selected for

TiGr7belongstoafamilyo fTiallovs especially designed to with standaggressive chemical enviro nments. The superior corrosion resistance of Tiand Tialloys is due to a thin, stable and tenacious of the superior corrosion resistance of Tiand Tialloys is due to a thin, stable and tenacious of the superior corrosion resistance of Tiand Tialloys is due to a thin, stable and tenacious of the superior corrosion resistance of Tiand Tialloys is due to a thin, stable and tenacious of the superior corrosion resistance of Tiand Tialloys is due to a thin, stable and tenacious of the superior corrosion resistance of Tiand Tialloys is due to a thin, stable and tenacious of the superior corrosion resistance of Tiand Tialloys is due to a thin, stable and tenacious of the superior corrosion resistance of Tiand Tialloys is due to a thin, stable and tenacious of the superior corrosion resistance of the superior corresponds to the superior corrosion resistance of the superior corresponds to the superior correspo xide nditions. ¹⁰Tiallovshavea filmthatformsrapidlyon Tiinairandwater, especially under oxidizing co broadrangeofapplicationascorrosionresistantmaterials. This includes seawater, wetchlorine, chlori n-5,10,11 Someofthemediain atedorganiccompounds and oxidizing acids (e.g. nitric and chromic acids). which Tishou Idnot be used include hydrofluoricacid, drychlorine and hot pure sulfuricacid sol utions. ¹³TiGr2(R50400)isco ¹²ThefamilyofTicorrosionresistantalloysincludesgradesfrom1to34. mmerciallyoneofthemostpopulargrades. Other, morecor rosionresistantgrades, which are the f ocusof thecu rrentstudy, includes TiGr7(R52400), TiGr16(R52402) and TiGr12(R53400) (Tables 1 and 2). These grades contain small amounts of alloying elements that improve the corrosion resistance of ¹⁴ Ti Gr7 contains titanium in reducing conditions by a mechanism called the cathodic modification. 0.12-0.25% palladium (Pd), Ti Gr 16 contains 0.04 -0.08% Pd and Ti Gr 12 contains 0.2 -0.4 molybd enum(Mo)and0.6 -0.9% nickel(Ni). ¹³Ingeneral, the corrosion resistanceofTiGr7issuperiortothat of Ti Gr 12; however, this effect is more noticeable under reducing conditions due to the beneficiale ffect of Pd. ⁵ Corr osion rate data for Ti Gr 16 are scarce. Some Ti allovs may be susceptible to crevice corrosion under certain conditions; however, these alloys are practically immune to pitting corrosion in ¹⁰Ithasbeensuggestedthatthesu halidecontainingenvironmentsundermost practical applications. sceptibilitytocrevicecorr osionisduetotheforma tion of low pH reducing solution under the occluded ¹⁵⁻¹⁶Halideandsulfate conditions, wherethe corrosion rate of Tiishigherthaninoxidizing conditions. ^{17,18}Bromide containingsol utionsmavinducecrevicecorrosioninTiattemperatureshigherthan70°C. ¹⁹Anodicpolarizations ionsseemmorea ggressivethanchlorideionsforthepassivitybreakdownofTi. orideandfluoridecontainingsolutionsat95°Chaveshownthatthepresenceoffluoride ofTiGr7inchl ²⁰Thepresenceoffluoride produces significantly higher current densities above the corrosion potential. ations. 20 mayhavealsorenderedTiGr7moresusceptibletocrevicecorrosionunderanodicpolariz

Titanium and Ti alloys may suffer environmentally assisted cracking (EAC) such as hydrogen embrittlement (HE) and stress corrosion cracking (SCC). Embrittlement by hydrogen is a consequence of a sorption of atomic hydrogen by the metal to form hydrides.

10,12,17,21-25 This may happen in service when the Ti alloyis coupled to a more a ctive metal in an acidic solution.

10 Acritical concentration of hydrogen in the metal may be needed for HE to occur.

23 The fewen vironments that can induce SCC in Ti are absolute (anhydrous) methanol, red -fuming nitricacid and nitrogen tetraoxide.

10-11,17,22,26-27 A few per cent of water in the environments mental may be needed by we would inhibit the SCC in Ti.

The susceptibility to stress corrosion cracking and hydrogenem brittlement of titanium and Tialloyshas been studied recently egarding its application for the Yucca Mountain repository. Royet al. performed slows train rate tests ($3.3 \times 10^{-6} \text{s}^{-1}$) on smooth specimens of TiGr7 and TiGr12 in 5 wt% NaClpH2.7 at 90°C at the applied potentials between 0 V and -1.2 V(SSC). They reported that for TiGr12 (R53400), as the potential decreased the reduction of area at rupture decreased from 40% at 0 V to a proximately 15% at -1.2 V(SSC). They attributed this behavior to a hydrogenem brittlement mech

nismduetotheformationofhydrides.Und erthesametestedconditionsthereductionofareaofTiGr7 (R52400)remained approx imately constant at near 50%. Royet al. reported that after straining, both Ti ²⁸Gre eneetal.calc u-Gr7andGr12exhibitedshallowsecondarycracksatallofthetestedpotentials. lated that the critical concentration of hydrogen to produce HE was higher in palladium containing tit a-²⁹Greeneet niumalloys(suchasTiGr7)thanfortitaniumalloyswithoutpalladium(suchasTiGr12). al. also anticipated that an en hanced passive corrosion rate of Ti Gr7 (for example in an environment containingfluorideions)couldpr oduceenoughhydrogentoreachthecriticalconcentrationinthemetal to cause HE. ²⁹ Pulvirenti et al. reported intergranular stress corrosion crack ing (IGSCC) changing to transgranular stress corrosion cracking (TGSCC) on one U -bend specimen of Ti Gr7 exposed for 155 ³⁰Younget daysinasolutioncontaining35,500ppmchlorideand1900ppmflu oridepH6.5at105°C. al.reportedstresscorrosioncra ckinginTiGr7specimenssubjectedtoconstantloadtestsinaconce ntratedgroundwatersolutionpH~10at105°C.

Watersthatcontactthedripshieldareexpectedtobeintheformofamulti -ionicsolution.Thissol ution mayformthroughtwodif ferentmechanisms:(1)Drippingfromthedriftwallandconcentratingonthe dripshieldsurfaceand(2)Deliquescenceofsalts(dust)thatmayaccumulateontopofthedripshield ated. The ground waters that duringdryperiods. Inbothcases, the aqueous solution would be concentr ^{32,33}Table3showsthe are associated with the Yucca Mountain region have been well characterized.compositionofasaturatedzonewater(fromawelldesignated,J -13) from near the repositor vsite. The wellwater, J -13. is near-neutralandbicarbonate -richwithsignificantconcentrations of sulfate, nitrate, chloride, alkalisandalkalineearthsions. Table 1 also shows the composition of various laboratory prepared, aqueous, concentrate delectrolytesolutions in which test ingwasperformed. These electrolyte solutionsrangefrompH~3to10andaredesignatedassimulatedacidifiedwater(SAW),simulated concentratedwater(SCW)andsimulateddilutewater(SDW).

Thepurposeofthepresentworkwastodeterminethestres scorrosioncrackingresistanceofTiGr7a f-termorethana2.5 -yearexposureandTiGr16andTiGr12aftermorethana5 -yearexposureinthe aboveme ntionedmulti -ionicsolutionsat60°Cand90°CusingU -bendspecimens.

EXPERIMENTAL

There are several different techniques that can be used in the laboratory to study the susceptibility of a loys to EAC. The techniques can be grouped by the way the mechanical stress is applied to the testing specimen. In order to better simulate the likely field behavior, the samples that are used for labor testing should reproduce closely the field conditions. The only mechanical stresses that may be prockfall impact. Therefore, the specimens chosen for laboratory testing were U-bend specimens, which also contained residual stresses due to fabrication or poss also contained residual stresses due to fabrication at ion.

The studied nickel alloys included Titanium Grade 7 (R52400), Titanium Grade 16 (R52402) a ndTit anium Grade 12 (R53400). Table 2 shows the compositions of the studied alloys. The welded U -bend specimenshadmatchingfillermetal, that is, a wire of the same allow was used to produce the welds (T able2). Inthe designation of the specimens, th efirstlettercorrespondedtothetypeofalloy. Thusanin itialletterNrepresentsTiGr7.theletterFrepresentsTiGr16andtheletterErepresentsTiGr12(Table 1). The second letter in the designation represents the type of specimen, in this c asetheletter Urepr esents U -bend. The third letter designates if the material for the U -bendwas seamless wrought mill a nnealed(MA)(letter A)orhada weldseam(letter different from A)(Figure 1 and Table 4). These three

lettersarefollowedbyathr ee-digitserialnumber. Thus, FUE079 is the welded TiGr 16U -bendspec imennumber 79.

The U-bend specimens were machined from sheet stock. The specimens were tested in the as -machined condition, which corresponded to a root mean square (RMS) roughness of 32 µ -inch. The specimens wered egreasedinacetonebeforetesting. The U -bendspecimenswerepreparedusing³/₄ -inch(~19mm) wideand 1/16 -inch(~1.6mm) thick strips according to ASTMG 30. The resulting specimenhadaco nstantnominalseparationbetwee nbothlegs, orends, of 0.5 inch (~13 mm) secured by abolt, which was electrically insulated from the specimenthrough ceramic zirconia washers. The total plastic deformation in the external outer fiber was approximately 12%. Single U -bends were produced u sing both wrought sheetsandweldedsheets.Intheweldedspecimens,theweldwasacrosstheapexofthebend(Figure 1). The weldprocess was gas metalar cwelding (GMAW) using filler metaland the seam had full penetr ation. Typical mechanical propertie sof MAsheet material are listed in T able1.Table2liststhechemical composition of the sheet material and the filler metal used for the fabricationoftheU -bendspecimens.

ThetestingelectrolytesolutionsfortheU -bendwere solutions containings everalionic species. The vo ume of the electrolytes was approximately 1000 liters. Table 3 shows the composition of the multi componentelectrolytesolutionsmentionedinthispaper. Table 3 also shows the composition of the w aterfromwellJ -13atYucca Mountain.The solutions used in this study are concentrated ve rsionsofJ -13 water. The U -bend immersion tests were carried out at 60°C and 90°C. A pproximately half of the specimenswereexposedtotheliquidphaseofthesolutionandtheotherhalftothe vaporphase.Ther ported te mperature corresponded to the liquid phase. The exposure time was approximately 5 years (the actual exposure time is given in Table 4) for TiGr 12 and TiGr 16 and approximately 2.5 years for Ti Gr 7. The electrolyte solutions were naturally aerated; that is, the solutions were not purged with any gas; however the ingress of air above the solution level was not restricted. All tests were carried out u nder ambient pressure. The specimens were tested at the free corrosion potenti al (E corr), that is, external polarization was not applied. The electrochemical potentials in this paper are reported in the saturated silver chloride scale [SSC]. At ambient temperature, the SSC scale is 199 mV more positive than the normalhydrogenele ctrode(NHE). Aftertesting, the specimens were studied using standard procedures suchasopticalandscanningelectronmicro scopy.

RESULTSANDDISCUSSION

ConstantDeformationTests(U -bendSpecimens)

The U-bend specimens were exposed to three different multi-ionic electrolyte solutions at the free corrosion potential (E $_{corr}$) for up to 5 years. Two of these electrolyte solutions (SCW and SDW) were alkaline of pH ~ 10 and one electrolyte (SAW) was acidic of pH ~ 3. One hundred and eighty two (182) specimens were removed from six of the testing tanks, rinsed in decomposition and allowed to dry in the laboratory atmosphere. Table 4 lists the specimens by their label, by the vessel they were a posed to and by the length of time they were tested. In general, three specimens were examined for each temperature, solution composition and metallurgical condition.

The 182 specimens were first examined optically in a stereomic roscope using up to 100 times magnific tion. Stereomic roscope studies showed that mo st of the specimens were completely featur they appeared shiny metallic similar to the non tested condition. Table 5 summarizes the office they appeared shiny metallic similar to the non for the different tested conditions. Most of the specimens had deposits of crystals (probably satisfied by the state of the specimens had deposits of crystals (probably satisfied by the state of the specimens had deposits of crystals (probably satisfied by the state of the specimens had deposits of crystals (probably satisfied by the state of the specimens had deposits of crystals (probably satisfied by the state of the specimens had deposite of

the electrolyte. The specimens that were exposed to the vapor phase had lower amount of d epositsthan the specimens exposed to the liquid phase. However, surface features suggest that the specimens e posed to the vapor phase had abundant condensa tion on them. The specimens that were tested at the highertemperature(90°C)intheliquidphaseingeneralshowedhigherdegreeofdiscolorationthanthe specimenstestedat60°C. This may suggest that there was more interaction between the specimens and the environment at the higher temperature; however, most of the colors and deposits observed (T able5) suggestthatthesewereresultofbuildupfromtheenvironmentratherthanduetoareactionofthemetal with the environment. Besidest it anium alloys ,thetankslistedinTables4and5containedalargenu mberofspecimensmadeofnickelalloyssuchasAlloy22,C -4,G-3,825and625.Theoriginoftheco lors (e.g. golden/green/blue) is not yet known (Figure 2). The golden color was probably caused by thed epositoflittlecrystalsofthiscoloronthesurface.Someofthesesmallcrystalsmayberichiniron.Some rust could have come from the dissolution of residual iron material transferred to the specimens and couponsduringtheirmechanicallabeli ngusingmetalstampsorpunches.

Someofthetested TiGr 12 specimens suffered minor corrosion and shallow fissuring, which nucleated from the side of the specimens, not from the apex or top. Some of this minor corrosion and fissuring (Figures 3 and 4B) could have initiated due to the presence of residual material or defects from fabric ation tools. None of the Ti Gr 16 and Ti Gr 7 specimens suffered environmentally assisted crac king (EAC).Figure6areSEMimagesoftwotestedTiGr7U -bendspecimenss howingtheabsenceofEAC. Of the 182 examined specimens listed in Table 4, only three suffered environmentally assisted cracking (EAC) or stress corr osion cracking (SCC). These were the welded Ti Gr 12 specimens exposed to the SCWliquidsolutionat90°C (Figure 4 Aand Figure 5). Ti Gr 12 in general is less resistant to corrosion than Ti Gr 7, especially under reducing conditions. For example, Schutz and Grauman measured the critical pitting temperature (CPT) of TiGr 12 and TiGr 7 in 47% MgCl 2 under an applied current de n-³⁴Theyr eportedthattheCPTofTiGr12was175°CwhiletheCPTofTiGr7was sityof200mA/cm². higherthan 260°C. ³⁴Moreover, TiGr 12 has higher strength and lower ductility than TiGr 7 or Gr 16 (Table 1); which could be detrime nt al for resistance to EAC. It has also been reported before that TiGr12suffered brittlementatcathodicappliedpotentialswhileTiGr7wasnotembrittledunderthesame testingcond itions. ²⁸

At this moment, it is not known if the environmental a ssisted cracking (EAC) of welded Ti Gr 12r eportedherewasaresultofstresscorrosioncracking(SCC)orhydrogenembrittlement(HE). The corr Osionpotential(E corr)oftitaniuma lloysunderthetestedconditionsisnotknown.E corrvaluesforAlloy22 show that these can range from approximately +0.35 V (SSC) in SAW at 90°C to near 0 V in SCW at 90°C. ³⁵Thatis, the E corr in SAW, where Ti Gr 12 did not suffer cracking, was higher than the E corrin SCW, where TiGr 12 did crack. Hence, is more likely tha thydrogencouldbedischargedinatomicform in the SCW solution, ingress the alloy and therefore cause embrittlement. On the other hand, SCW co ntained1400ppmoffluorideinitscomposition(Table3)andSAWdidnotcontainanyfluoride. Thisa n-²⁰Additio nioncoul dincreasethecorrosionrateofTitaniumalloysbypartiallydestroyingitspassivity. ³⁰Itisalsoimpo ally, it has been reported that Ti Gr7 cracked in a solution containing fluoride ions. tant to mention that only the welded Ti Gr 12 spec imenscrackedin SCW liquidat 90°C. Non -welded specimensthatwereimmersedsidebysidewiththeweldedspecimenswerefreeofEAC(Table4). This effect could be related to the mechanical properties of the welded seam as compared to a seamless specimen. Welds tend to have higher strength and lower ductility than the base material, therefore b ecomingmoresusceptibletoEAC.

ResultsfromthistestingshowthatoneofthetestedTialloyssufferedcrackinginonlyoneenv ironment. TiGr12canbeconside redtheleastcorrosionresistantofthethreetestedalloys.ThePdcontaininga l-

loys, both TiGr16 and TiGr7, were free from cracking in all the tested conditions. These results show that non-welded (wrought) and welded TiGr16 and TiGr7 are highly resistant to EAC when exposed to the free corrosion potential in a cidic and alkaline multi ionic solutions that could be representative of concentrated Yucca Mountain ground water.

RELATIVECORROSIONRESISTANCEOFTITANIUMALLOYS

Asmentioned introduction, corrosion resistant titanium alloys have different response to corrosive environments depending on their alloying elements. Commercially pure titanium or Ti Gr 2 (R50400) practically does not contain any metallic alloying element. Titanium Gr 12 contains approximately one percentofbothMoandNiandTiGr7containsabout0.15%Pd(Table2).Thesmallamountofmetallic alloying elements in titanium increases its corrosion resistance under acidic reducing conditions by the cathodic modificat ion mechanism. That is, these small amounts of alloying elements shift the corrosion potential of the titanium allovin the anodic direction favoring its passivation. Metallical loving elements are not as beneficial under oxidizing conditions since in thi scasetheenvironmentprovidesthedriving forceforoxidefilmformation. On the other hand, the metallical loying elements also decrease the su Sceptibility of titanium alloys to crevice corrosion, basically by reducing the corrosion rate of the alloy underthereducing conditions of an active crevice in an occluded cell. It is also commonly accepted that allovs that offer resistance to localized corrosion such as crevice and pitting corrosion are also resi stant to stress corrosion cracking; another loc alized corrosion process. Palladium and other platinum group metals (PGM) seem to be the most beneficial metallic elements to promote the cathodic modification restmentioned in this paper (TiGr7, TiGr16 and T mechanism. That is, for the alloys of inte iGr12), TiGr7, with 0.15% Pd(Table 2) would offer the highest corrosion resistance, TiGr 16 the inte rmediate and TiGr12 the lowest since it contains Mowhich is not part of PGM. Corrosion rated at a for TiGr16 are scarce; therefore the analysis o fcorrosionratewillbedoneusingTiGr2,Gr12andGr7.Figure7 shows the corrosion rates of Ti Gr 2, Gr 12 and Gr 7 in boiling dilute solutions of sulfuric and hydr Ochloricacid (reducing conditions). Due to the beneficial alloying properties of Pd, thecorrosionrateof Ti Gr 7 is approximately two orders of magnitude lower than the corr osion rate of Ti Gr 12. Figure 8 shows the corrosion rate of the three titanium alloys in two versions of the same oxidizing acidic sol uin ASTMG28B contains 23% H tion. The solution mentioned 2SO₄ + 1.2% HCl + 1% FeCl 3 + 1%2SO4+1.2% HCl+1% FeCl CuCl₂andthegreendeathsolutioncontains11.5%H 3+1%CuCl 2.Figure 8 shows that the corrosion rates of the three titanium alloys are of the same order of magnitude.Thatis, inoxidizingconditions, the beneficial effects of alloying Pdared iminished. Figure 8 shows also that the corrosion rate of the titanium alloys was higher in the ASTMG28B solution than in the green death environment, probably due to the highe racidconcentrationintheformer.

Wongetal.recentlyreportedcorrosionratedataforTiGr12,Gr16andGr7after5and2.5yearsi m-mersiontestsinSAW,SCEandSDWsolutionsat60°Cand90°C. ³⁶Ingeneral,TiGr12exhibitedthe highestcorro sionrates andTiGr7thelowest.Forexample,thecorrosionrateofcrevicedTiGr12in liquidSCWat90°Cwas192nm/yearandthecorrosionrateofTiGr7inthesameconditionswas32 nm/year.ThemostaggressivesolutionfortitaniumalloyswasSCW (concentratedalkaline)andtheleast aggressivewereSDW(dilutealkaline)andSAW(concentratedacidic). ³⁶

CONCLUSIONS

- (1) Millannealed (MA) or wrought and welded Ti Gr7 and Ti Gr16 alloys are highly resistant to environmentally assisted cracking (EAC) in multi-ionic solutions that could be representative of groundwater at Yucca Mountain.
- (2) U-bendsamplesofTiGr16exposedatE _{corr}forupto5yearsandTiGr7exposedfor2.5years inSAW,SCWandSDWsol utionsat60°Cand90°Cwerefre efromEAC.
- (3) WeldedTiGr12U -bendspecimenssufferedEACinSCWliquidat90°C.Underthesameco n-ditions,non -weldedTiGr12wasfreefromcracking.

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TABLE1
TYPICALMECHANICALPROPERTIESOFTITANIUMALLOYSSHEET
(FromASTMB265)

Alloy,UNS	FirstLetterNot a- tionforSpec i- mens	TensileStrength min.[UTS] (MPa)	YieldStress [0.2%]min. (MPa)	Elongationto Rupturemin.(%)
TiGr7,R52400	N	345	275	20
TiGr 16,R52402	F	345	275	20
TiGr12,R53400	E	483	345	18

NA=NotAvailable

 $TABLE2 \\ CHEMICAL COMPOSITION OF TITANIUM ALLOYS (Wt\%)$

	TiGr7	TiGr7	TiGr16	TiGr16	TiGr12	TiGr12
	BaseMetal	WeldFiller	BaseMetal	WeldFiller	BaseMetal	WeldFill er
Heat	R3928	BN4591	X-52020	5D3438	BN2966	AT7879
C	0.07	0.008	0.013	0.008	0.05	0.006
H	0.003	0.002	0.0048	0.0063	0.002	0.0044
Fe	0.18	0.02	0.11	0.04	0.07	0.12
Mo					0.36	0.3
N	0.011	0.008	0.006	0.002	0.02	0.004
Ni					0.78	0.82
O	0.12	0.037	0.14	0.12	0.14	0.08
Pd	0.16	0.17	0.07	0.19		
Ti	>99	>99	>99	>99	>98	>98

 $TABLE 3 \\ CHEMICAL COMPOSITION OF THE ELECTROLYTES OLUTIONS (mg/L)$

Ion	SDW	SCW	SAW	J-13WellW ater
	pH10.1	pH10.3	pH2.8	pH7.4
K ⁺	34	3400	3400	5.04
Na ⁺	409	40,900	40,900	45.8
Mg^{2+} Ca^{2+}	1	<1	1000	2.01
Ca^{2+}	0.5	<1	1000	13
\mathbf{F}^{-}	14	1400	0	2.18
Cl	67	6700	24,250	7.14
NO_3	64	6400	23,000	8.78
$\mathrm{SO_4}^{2\text{-}}$	167	16,700	38,600	18.4
HCO_3^-	947	70,000	0	128.9
SiO_2 (aq)	~40	~40	~40	61.1

TABLE4
LISTOFCONSTANTDEF ORMATION(U -BEND)EX AMINEDSPECIMENS

	SAW,	SAW,	SCW,	SCW,	SDW,	SDW,
	60°C	90°C	60°C	90°C	60°C	90°C
Vessel	25	26	27	28	29	30
Datein	06Feb1997	21Feb1997	10Mar1997	10Apr1997	14Apr1997	05Jun1997
Dateout	20May2002	21May2002	17May2002	22May2002	10May2002	22May2002
Exposure	1930	1916	1895	1869	1853	1813
Time,days(h)	(46,320h)	(45,984h)	(45,480h)	(44,856h)	(44,472h)	43,512h)
•						
Gr7Datein	20Dec1999	16Dec1999	19Dec1999	14Dec1999	09Dec1999	07Dec1999
Gr7 Dateout	20May2002	21May2002	17May2002	22May2002	21May2002	22May2002
Gr7Exp osure	882	887	883	890	894	897
Time,days(h)	(21,168h)	(21,288h)	(21,192h)	(21,360h)	(21,456h)	(21,528h)
Wrought -V a-	NUA001-003	NUA031-033	NUA061-063	NUA091-093	NUA121-123	NUA151-153
porPhase	FUA019-021	FUA049-051	FUA079-081	FUA109-111	FUA127	FUA139
r	EUA019-021	EUA049-051	EUA079-081	EUA109-111	EUA127	EUA139
Wrought -	NUA028-030	NUA058-060	NUA088-090	NUA118-120	NUA148-150	NUA178-180
LiquidPhase	FUA022-024	FUA052-054	FUA082-084	FUA112-114	FUA128	FUA140
1	EUA022-024	EUA052-054	EUA082-084	EUA112-114	EUA128	EUA140
Welded- V a-	NUE013-015	NUE043-045	NUE073-075	NUE103-105	NUE133-135	NUE163-165
porPhase	FUE019-021	FUE049-051	FUE079-081	FUE109-111	FUE127	FUE139
1	EUD019-021	EUD049-051	EUD079-081	EUD109-111	EUD127	EUD139
Welded- Li q-	NUE016-018	NUE046-048	NUE076-078	NUE106-108	NUE136-138	NUE166-168
uidPhase	FUE022-024	FUE052-054	FUE082-084	FUE112-114	FUE128	FUE140
	EUD022-024	EUD052-054	EUD082-084	EUD112-114*	EUD128	EUD140
TotalExa m-	36	36	36	36	20	20
inedSpec i-						
mens						
TotalCracked	0	0	0	3	0	0
-						

^{*}Thesearetheonlyspecimensthatcracked.

TABLE5
STEREOMICROSCOPEOBS ERVATIONSOFTHETES TEDU -BENDSPECIMENS

Conditions	VaporPhase	LiquidPhase		
Vessel25	Shinygraymetallic.Fewisolatedbrown	Shinygray -greenorlightgolden.Small		
SAW,60°C	deposits.SomecorrosiononedgesforGr	amountofbrowndeposits.Noco rrosion.		
	12.Nocracking	Nocracking		
Vessel26	Shinymetalliclightgray orbluish.Brown	Goldenbrownwithagreentint.Somefi s-		
SAW,90°C	depositsinconcavearea.Noco rrosion.	suresfromedgesonTiGr12.Nocorr o-		
	Nocrac king	sion.Nocracking		
Vessel27	Shinyanddulllightgraywithbluishand	Shinylightgoldenandgray.Shallow		
SCW,60°C	goldenpatches.Whitede posits.Nocorr o-	cracksfromsideandcorrosiononleg		
	sion.Nocracking	ends(Gr12).Nocorrosion.Nocrac king		
Vessel28	Shinydarkgrayandgolden.Littlewhite	Samplecoveredbywhitedeposits.No		
SCW,90°C	andgreendepositsinconcavearea.No	apparentcorrosion.Nocracking. Welded		
	corrosion.Nocracking	TiGr12Cracked(EAC).		
Vessel29	Shinylightgrayandgolden.Littlecorr o-	Shinylightgrayandgolden. Littlecorr o-		
SDW,60°C	sionatendoflegsforGr12.Nocracking	sionfromsidesforGr12.Nocracking		
Vessel30	Shinygrayandlightgolden.Littlecorr o-	Shinygray,blueandgolden.Shallowco r-		
SDW,90°C	sionfromsidesforGr12.Nocracking	rosionfromsidesforGr12.Nocracking		

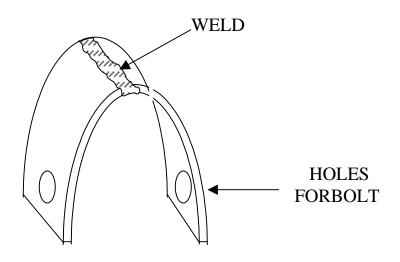
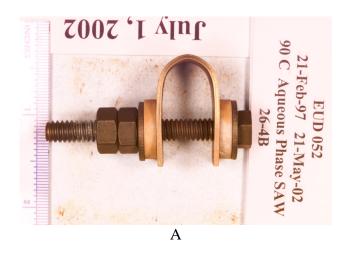
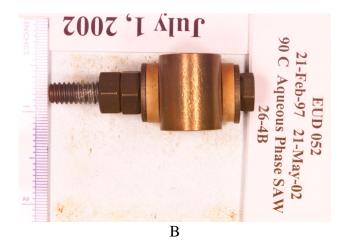
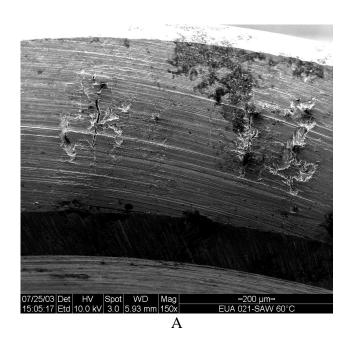


FIGURE1:SchematicrepresentationoftheweldedU -bendspecimens.





 $FIGURE2: Welded TiGr12 exposed for 5+ years in SAW liquid at 90 ^{\circ}C, (A) Sideview and (B) topor a pexview. The specimen is free from cracking.$



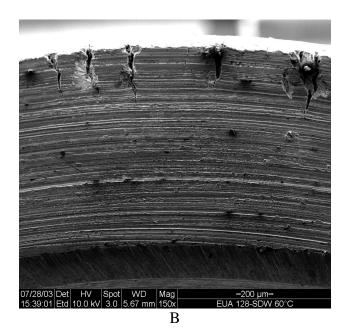
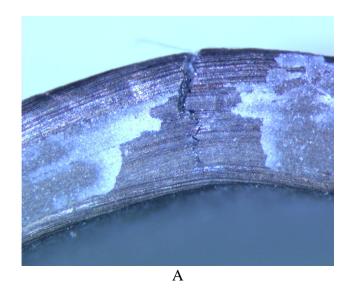


FIGURE3:Sideviewofnon -weldedTiGr12U -bendspecimensexposedfor5+yearsintheLTCTF. (A)EUA021inSAWvaporat60°C,150XMagnification and (B)EUA128inSDWliquidat60°C,150XMagnification Thespecimenssufferedminorfissu ring.



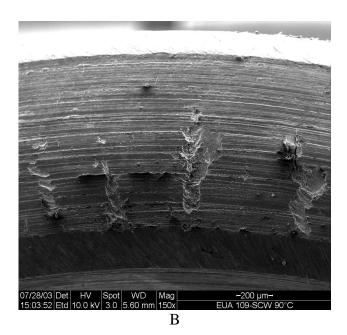
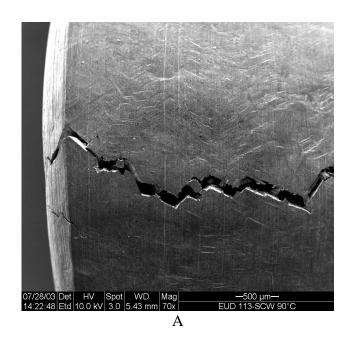


FIGURE4:Sideviewofnon -weldedTiGr12U -bendspecimensexposedfor5+yearsintheLTCTF.

(A)EUD112inSCWliquidat90°C,approximatelyX20Magnification and

(B)EUA109inSCWvaporat90°C,X150Magnification

OnlytheweldedTiGr 12specimensinexposedtotheliquidphaseofSCWat90°Csufferedsevere cracking(Figure5).Thenonweldedspecimenintheliquidphasesufferedminorfi ssuring.



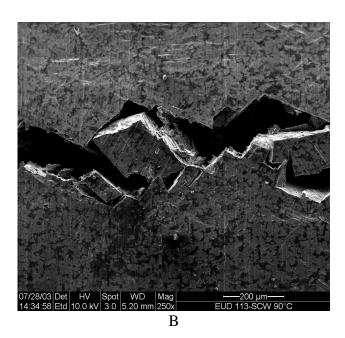
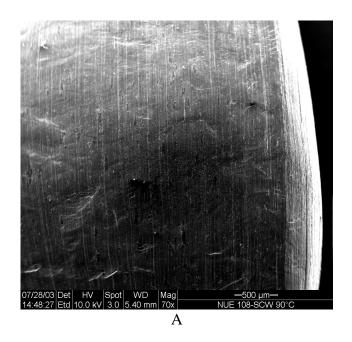


FIGURE5:Topview(apex)SEMimagesofweldedTiGr12(EUD113)exposed liquidat90°C.(A)X70Magnificationand(B)X250Magnification.
Thespecimensufferedenvironmentallyassistedcracking.

for 5+ years in SCW



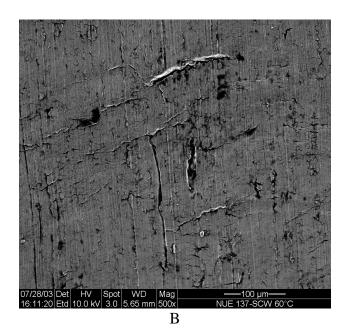


FIGURE6:Topview(apex)ofweldedTiGr7U -bendspecimensexposedfor2.5+yearsintheLTC TF.

(A)NUE108inSCWliquidat90°C,X70Magnification,and

(B)NUE137inSDWliquidat60°C,X500Magnific ation.

Allthenon- weldedandweldedTiGr7specimenswerefreefromenvironmentallyassistedcrackingin allthetestedenvironments.Somemino rfissuringobservedintheapexispre -existenttotesting.

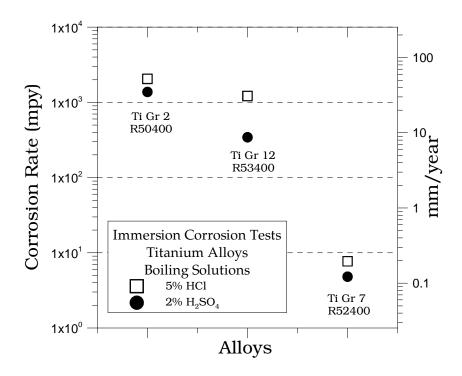
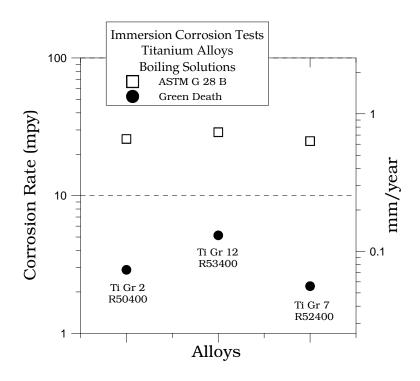


FIGURE7: Corrosion Rate of Tialloys in reducing a cidic conditions. The corrosion rate of TiGr7 is several orders of magnitude lower than the corrosion rate of Data from Haynes International and Reference 5.

fTiGr12.



 $FIGURE8: Corrosion Rate of Tialloys in oxidizing a cidic conditions. \\ ASTMG28B contains 23\% H _2SO_4 + 1.2\% HCl + 1\% FeCl _3 + 1\% CuCl _2 and the green death solution on contains 11.5\% H _2SO_4 + 1.2\% HCl + 1\% FeCl _3 + 1\% CuCl _2. \\ Inboth solutions, the corrosion rates of TiGr7 and TiGr12 are comparable. \\ Data from Haynes International and Reference 5. \\ \\$